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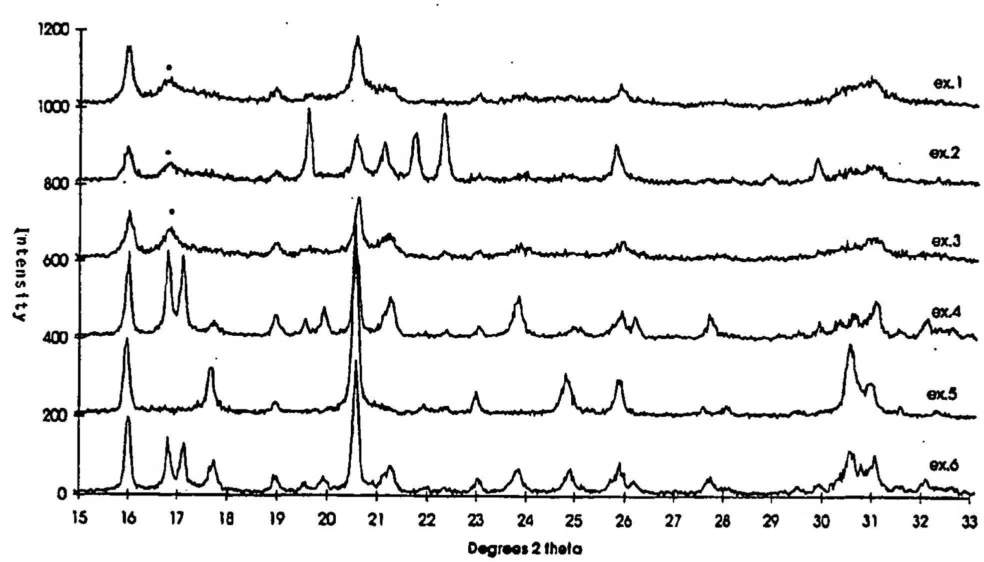

(57) Abstract

The invention concerns microporous crystalline silico-alumino-phosphate (SAPO) compositions, catalytic materials comprising said composition, and use of these for production of olefins from methanol. The catalysts comprise silico-alumino-phosphate materials with AEI/CHA-mixed phase composition. The invented catalysts have prolonged life compared to those belonging to the prior art.

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"A MICROPOROUS CRYSTALLINE SILICO-ALUMINO-PHOSPHATE COMPOSITION, CATALYTIC MATERIAL COMPRISING SAID COMPOSITION, AND USE OF THESE FOR PRODUCTION OF OLEFINS FROM METHANOL".

The invention concerns catalysts for methanol to olefins comprising silico-alumino-phosphate (SAPO) materials with AEI/CHA-mixed phase composition.

From Norwegian Patent No. 169 380 (corresponds to US-A- 4 440 871) microporous crystalline silico-alumino-phosphates are known and a procedure for synthesising such products. These products have a three-dimensional space lattice built up from PO_2+, AlO_2- and SiO_2 tetrahedral units, whose most important chemical composition on a water-free basis is:

$$mR{:}(Si_xAl_yP_z)\,O_2$$

where "R" represents at least one organic template material which is present in the intracrystalline pore system; "m" is the number of moles of "R" present per mole of $(Si_xAl_yP_z)\,O_2$ and m has a value between 0 and 0.3, the maximum value in each case being dependent on the molecular dimensions of the template material and the available pore volume in the silico-alumino-phosphate structure in question; "x", "y" and "z" are molar fractions of silicon, aluminium and phosphorus respectively, present as tetrahedral oxides. The minimum value of "x", "y" and "z" is 0.01, and the maximum value of "x" is 0.98, of "y" 0.6 and of "z" 0.52. The minimum value of "m" in the formula above is 0.02.

The reaction mixture is achieved by combining at least one part each of the aluminium and phosphorus sources in the absence of the silicon source. Then the resultant mixture is reacted with the remaining components to get the total reaction mixture.

The reaction mixture is placed in a pressure vessel for shaking and then heating under autogenic pressure to a temperature of at least 100°C, and preferably between 100 and 260°C, until a crystalline silico-alumino-phosphate is obtained. The product is extracted in any appropriate way, for example by centrifuging or filtering.

From our own Norwegian Patent No. 174341 an improved method of producing silico-alumino-phosphate catalysts for the conversion of methanol into light olefins such as ethylene and propylene (the MTO reaction) is known. The improved method of synthesis can be used to control chemical composition of the silico-alumino-phosphates, especially the silicon content. In particular, it was found that catalysts that are more stable towards deactivation by "coking" can be synthesised, which is very important for the design of an MTO process based on the synthesised silico-alumino-phosphates.

From our own Norwegian Patent Application No. 932915 a microporous crystalline silico-alumino-phosphate with theoretical composition on a water-free basis after synthesis and calcination:

$$H_xSi_xAl_yP_zO_2$$

where x has a value between 0.005 and 0.1 and y and z are values between 0.4 and 0.6, is known. The product has AEI-structure and has acidic properties. The product is useful as sorbent and as catalyst for olefin production from methanol.

A problem related to all the catalysts known from the above mentioned prior art is that the lifetime of the catalysts is limited.

Thus, a main object of the invention is to produce a catalyst with prolonged life compared to those belonging to the prior art.

This object and other objects of the invention are achieved as defined in the patent claims listed at the end of this application.

The present invention concerns a crystalline silico-alumina-phosphate microporous material containing at l ast the two phases AEI and CHA, the theoretical, average chemical composition of which, on a water-free base after synthesis and calcination, is:

$$H_xSi_xAl_yP_zO_2$$

where x has a value between 0.005 and 0.1 and y and z are values between 0.4 and 0.6, and "x", "y" and "z" are mol fractions of silicon, aluminium and phosphorous respectively, present as tetrahedric oxides. The present invention further concerns the use of said material for the production of light olefins from methanol, for which said material surprisingly has been found to be superior to materials of the same chemical composition with either pure AEI or pure CHA phase, as illustrated in examples below.

The manufactured catalytic material, called RUW-19, consists of small, irregularly shaped particles which, after calcination in air at 550°C for 4 hours, produce a characteristic x-ray diffractogram which at least includes the reflexes stated in Table 1, all of which are reflections characteristic of either the AEI-phase, the CHA-phase or both phases, and from which the reflection between 2 theta = 9.3 and 9.5 is always the strongest.

TABLE 1

2θ	d(Å)
9.3 - 9.5	9.3 - 9.4
10.4 - 10.6	8.3 - 8.5
12.7 - 12.9	6.8 - 7.0
13.8 - 14.0	6.3 - 6.4
15.9 - 16.1	5.5 - 5.6
16.7 - 16.9	5.2 - 5.3
18.9 - 19.0	4.6 - 4.7
20.5 - 20.7	4.3 - 4.4
21.0 - 21.3	4.1 - 4.3
23.7 - 24.0	3.7 -3.8
25.7 - 26.0	3.4 - 3.5
30.9 - 31.1	2.8 -2.9

The product has acidic properties as demonstrated by the fact that > 0.05 mmoles NH_3/g material sorbed at 100°C is desorbed at temperatures > 300°C when it is heated in flowing helium at a ramp rate of 10°C/min.

The content of Si in the calcined product is in the range between 0.2 and 3 % weight, preferably between 0.4 and 1.2. The manufactured product has pore openings and channels of 4 - 5Å diameter, and cavities, the smallest size of which is > 5 Å, as found for both the AEI- and the CHA-structures.

RUW-19 is manufactured from a mixture of reactive sources of SiO_2, Al_2O_3 and P_2O_5 and an organic template material. Said mixture is manufactured by combining at least one portion of the Al-source and the P-source with water, the Si-source and the organic template material. The reagents can be added in different orders and quantities, and from different sources, but Al-isopropoxide, phosphoric acid, colloidal silica and tetraethylammonium hydroxide have proved to be particularly useful sources of Al, P, Si and organic template material, respectively. It has further proved convenient to mix the

Al-source with the P-source and water first, and thereafter adding either the Si-source or the organic template material and finally the remaining reagent. The Si-source may also be dissolved in the organic template solution prior to blending with the other reagents. It is convenient to stir or shake the mixture between each addition, but this is not necessary. All the reagents may well be added before stirring or shaking starts. After so preparing the precursor gel it is put into a steel autoclave and after a short or long ageing period at room temperature the autoclave is heated to a maximum temperature between 180 and 260°C, for at least 1 hour, and preferably for more than 2 hours. It is important that the autoclave is either shaken, stirred or rotated during the entire process of ageing and crystallisation.

RUW-19 comprises as major constituents at least the two silico-alumino-phosphate phases with AEI- and CHA-structures, and the material is not well defined regarding the ratios between the different phases. Any silico-alumino-phosphate prepared in one batch crystallisation exhibiting x-ray-reflections characteristic of both phases AEI and CHA are defined as RUW-19 catalytic material. This means in practice that the ratio between the two phases are always between 0.1 and 10, because otherwise the identification of the minor constituent becomes uncertain. Physical mixtures of the two phases AEI and CHA prepared by mixing samples of the two pure materials are not defined as RUW-19.

Typically, RUW-19 is obtained as a product in preparations where some of the critical parameters of a SAPO-34-synthesis (see comparative example 5) is combined with some critical parameters of a SAPO-18-synthesis (see comparative example 4). This does not imply however that RUW-19 is always obtained in such preparations. RUW-19 is obtained only when certain critical parameters of a typical SAPO-34-preparation is combined with certain critical parameters of a typical SAPO-18-preparation, as described and exemplified below. In addition to this there are also some features characteristic of a typical RUW-19 preparation which are not found in typical preparations of SAPO-34 nor of SAPO-18, such as relatively short synthesis times and relatively high synthesis temperatures and the special decantation step described i example 1 and other minor details as can be seen from the examples and the comparative examples and other relevant publications in the field.

SAPO-18 / SAPO-34 mixed phase materials can generally be obtained in a much wider range of synthesis conditions than the two pure phases, but not all mixed phase samples are necessarily "long life - low coke" MTO-catalysts.

SAPO-18 / SAPO-34 mixed phase MTO-catalysts are obtained by including one or two, but not all three, of the following synthesis steps 1-3, departing from a typical SAPO-34 synthesis as described in the second comparative example (Example 5). If non of these steps are included a pure SAPO-34 will result, and if steps (1 - 3) are performed, a pure, or nearly pure SAPO-18 is obtained.

1. Water and phosphoric acid, and optionally HCl should be added to the Al-isopropoxide one by one, with mixing between each addition. (Column 4 in Table 8).

2. SiO_2-content in the gel should be below 5%, i.e. Si/(Al+P+Si)<0.05, and preferably below 0.04 and above 0.01, and most preferably between 0.015 and 0.025. (Column 2 in Table 8). The preferred silica source be a colloidal silica sol.

3. After addition of the silica source the amount of liquid in the gel should be reduced by one or more of the following methods; a) filtration, or b) drying or c) discharge of supernatant after sedimentation. (Column 6, 7 and 8 in Table 8).

   Some further synthesis steps favour the crystallisation of mixed phases when not all three of the above steps are performed. These additional steps are as follows;

4. Cooling of the gel under running water while shaking bottle gently. (Column 5 in Table 8).

5. Crystallisation temperature (set point on T-controller) should be at least 200°C but preferably as high as in the 250 to 260°C-range. Pure phases are preferably made in the 200 to 230°C-range. (Column 9 in Table 8).

6. Crystallisation time should be shorter the higher th temperature. In the 250 to 260°C-range the time should preferably be from 2 to 5 hours. Pure phases require a longer crystallisation time at lower temperatures. (Column 10 in Table 8).

A characteristic of the mixed phase samples in general is that they contain more than one crystalline phase which can be identified by XRD. Not all such mixed phases are as good MTO-catalysts as the mixed phase samples described in the present invention. The best samples, i.e. the samples with the longest catalytic lifetime (defined as described in Example 1 - 3) and the lowest overall coke selectivity have certain characteristics in common, that other mixed phase samples do not have. One such characteristic is that they contain at least the phases SAPO-18 and SAPO-34, and may also contain other phases such as SAPO-5 having the AFI-structure, or dense phases in limited amounts.

Another such characteristic is that they have XRD-profiles with only one broad feature in the region between 16.6 and 18 degrees 2 theta as illustrated in Fig. 1, marked with an asterisk. Pure phases (Example 4 and 5) and post-synthesis prepared mixed phase samples (Example 6) do not have such a broad feature, but have instead at least one relatively sharp peak in the same region.

The invention is further explained in the examples and figure below.

Fig. 1 shows the XRD-traces of the 15 - 33 degrees 2 theta region for the products of examples 1 - 6.

Example 1-3 show synthesis of SAPO-18/SAPO-34 -"intergrowths" according to the invention. Example 4-6 are comparative examples.

X-ray diffraction was performed on a Siemens diffractometer type D 5000 with Ni-filtered CuK-radiation and run in stepscan mode with steps 0.02 degrees and 1 sec. collect time per step. The intensities in Tables 2 - 7 have been given in letter codes according to the following scale:

Letter code	Intensity (counts)
vvs	> 1000
vs	500 - 999
s	250 - 499
m	100 - 249
w	40 - 99
vw	< 39

Identification and quantification of the different phases;

The AEI and CHA phases were identified and semi-quantified by XRD. For quantification the heights of two diagnostic peaks were measured; the 5.5Å-peak for the CHA-phase and the 5.2Å-peak for the AEI-phase, and divided by the heights of the same peaks in pure samples (Example 4 and 5), arbitrarily assessed 100% crystalline. The quantities of the different phases in the examples and otherwise in the text are thus always to be understood as determined according to this operational method. In the examples the percentages given refer to the sum of the crystalline material, whereas the values given in table 9 refer directly to the peak intensities compared to Example 4 and 5.

Example 1

(MTO-RUW-356.)

An aluminium phosphate-gel was first prepared by adding 212 g of a solution consisting of 55 g 85% H_3PO_4 and 151 g distilled water and 6 g HCl to 109 g of Al-isopropoxide in a 1 litre plastic bottle. The mixture was shaken for one minute, and then transferred to a closed Büchner funnel and evacuated by water suction. The mixture started to boil, and

was left to dry for 19 hours, so its weight was reduced from 321 to 135 g. Thereafter 156g 40% TEAOH was added, shaken for one minute and thereafter 4 g of Ludox LS was added and again shaken for one minute, resulting in a gel with the composition, expressed in terms of the molar oxide ratios, excluding water and isopropanol:

$0.79\ TEA_2O : 1\ Al_2O_3 : 0.075\ SiO_2 : 0.89\ P_2O_5$

The gel was thereafter stirred for one hour with magnetic stirrer. The resulting mixture, weighing 293 g was equally divided in 3, and one third was transferred to a Teflon lined autoclave. The autoclave was then put in an Al-heating block, and heated to 260°C. After 2 hours the autoclave was withdrawn and immersed in water for cooling. The content was centrifuged, and the solid redispersed in distilled water once, and again centrifuged (3600 rpm). The sediment was dried at 100°C over night. Dry weight of the solid product was 8.4 g, which was only about 50 % of the used reactants, on oxide basis. A portion of the product was calcined in dry air at 550°C for 5 hours. After calcination, the silico-alumino-phosphate mixed phase product has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 2 below.

Table 2:

2θ	d(Å)	I
9.41	9.39	vvs
10.55	8.38	w
12.83	6.90	m
13.30	6.65	w
13.89	6.37	vw
15.96	5.55	m
16.77	5.28	w
18.94	4.68	w
19.62	4.52	vw
20.55	4.32	m
21.17	4.19	w
23.04	3.86	w
23.81	3.73	vw
25.89	3.44	w
30.99	2.88	w

The X-ray diffraction analysis revealed that the crystalline product was composed of approximately 60 % SAPO-34 and 40 % SAPO-18.

The composition of the solid, calcined product was established, by means of chemical analysis, as

46.6 % Al_2O_3, 5.0 % SiO_2, 48.4 % P_2O_5,

which produced a product composition, with regard to the main components, of $Si_{0.05}Al_{0.54}P_{0.41}O_2$. These results showed that Si was enriched in the crystalline product as compared to the composition of the gel.

Example 2

(MTO-RUW-305.)

An aluminium phosphate-gel was first prepared by adding a solution of 15.4 g of 85% phosphoric acid, 0.4 g of 37% HCl and 36.7 g of distilled water to 27.2 g of aluminium isopropoxide in a 1/4 litre PE-bottle. The bottle was shaken for 1 minute. Next 1.1 g of Ludox LS colloidal silica was added, and the bottle was again shaken for 1 minute. Then 49.2 g of 40% TEAOH was added. The composition of the gel, expressed in terms of the molar oxide ratios, was:

$$1\ TEA_2O : 1\ Al_2O_3 : 0.08\ SiO_2 : 1\ P_2O_5 : 59\ H_2O : C_3H_7OH.$$

The bottle was shaken for 1 minute, and left standing for 1/2 minute resulting in a separation of phases in the gel. 25 ml of the relatively clear supernatant was discharged and the rest of the mixture was transferred to a teflon-lined autoclave, which was put in an aluminium heating block on a shaking-board at 90°C for 2 hours whereafter the temperature was increased to 260°C, and the mixture was heated for 4 hours at this temperature. After cooling the product was washed with distilled water and centrifuged. The sediment in the centrifuge tube was dried at 100°C over night.

A portion of the product was calcined in dry air at 550°C for 5 hours. After calcination, the silico-alumino-phosphate mixed phase product has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 3 below.

Table 3:

2θ	d(Å)	I
7.33	12.05	vvs
9.42	9.33	vvs
10.51	8.41	w
12.78	6.92	m
13.86	6.38	vw
14.77	5.99	w
15.97	5.54	w
16.82	5.27	w
18.96	4.68	vw
19.60	4.53	m
20.56	4.32	m
21.11	4.20	m
21.72	4.09	m
22.30	3.98	m
23.94	3.71	vw
25.79	3.45	m
28.95	3.08	vw
29.86	2.99	w
31.02	2.88	w
34.36	2.61	w
35.72	2.51	vw
37.79	2.38	vw

The X-ray diffraction analysis revealed that the crystalline product was composed of approximately 33 % SAPO-5, 22 % SAPO-34 and 28 % SAPO-18, and an additional 17 % of other phases.

Example 3

(MTO-RUW-335T.)

An aluminium phosphate-gel was first prepared by adding a solution of 61.6 g of 85% phosphoric acid, 0.8 g of 37% HCl and 146.8 g of distilled water to 109 g of aluminium isopropoxide in a 1 litre PE-bottle. The bottle was shaken for 1 minute and was left for 15 minutes whereafter it was filtered (water suction / black ribbon paper) for 15 minutes. The solid residue was then put in an oven at 100°C resulting in a dry material with a total weight of 100 g. 50 g of this dry material was added to a mixture of 39.4 g of 40% TEAOH and 2 g of Ludox LS-30 which had been stirred over night. The composition of the gel, expressed in terms of the molar oxide ratios, excluding water and isopropanol, was:

$0.4\ TEA_2O : 1\ Al_2O_3 : 0.075\ SiO_2 : 1\ P_2O_5$.

The resulting gel was shaken for 1 minute and then transferred to a teflon-lined autoclave, which was put in an aluminium heating block on a shaking-board at 90°C for over night whereafter the temperature was increased to 260°C, and the mixture was heated for 4 hours at this temperature. After cooling the product was washed with distilled water and centrifuged. The sediment in the centrifuge tube was dried at 100°C over night, in the tube. When recovered it was discovered that the dry product consisted of a relatively coherent top layer and a relatively powdery bottom layer, and the two layers were separated.

A portion of the top layer of the dry product was calcined in dry air at 550°C for 5 hours. After calcination, the silico-alumino-phosphate mixed phase product has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 4 below.

Table 4:

2θ	d(Å)	I
7.32	12.07	w
9.44	9.36	vvs
10.53	8.40	w
12.85	6.89	m
13.34	6.63	w
13.86	6.39	vw
16.02	5.53	m
16.84	5.26	w
18.97	4.67	w
20.60	4.31	m
21.20	4.19	w
22.34	3.98	vw
23.00	3.86	vw
23.86	3.73	w
25.91	3.44	w
27.86	3.20	vw
31.04	2.88	w

The X-ray diffraction analysis revealed that the crystalline product was composed of approximately 63 % SAPO-18, 33 % SAPO-34 and 3 % SAPO-5.

The composition of the solid, calcined product was established, by means of chemical analysis, as

47.7 % Al_2O_3, 3.5 % SiO_2, 48.8 % P_2O_5,

which produced a product composition, with regard to the main components, of $Si_{0.035}Al_{0.556}P_{0.409}O_2$.

Example 4.

(SAPO-18.)

(a) 108 g of distilled water was added to 81.6 g of aluminium isopropoxide in a 1/2 litre PE-bottle. The bottle was shaken for 1 minute. 45 g of 85% phosphoric acid was added,

and the bottle was shaken for 1 minute while cooled by running tap-water. Then 0.6 g of 37% HCl was added, and the bottle was again shaken for 1 minute while cooled by running tap-water. Next 3.0 g of Ludox LS colloidal silica was added, and the bottle was again shaken for 1 minute while cooled by running tap-water. The bottle was then left for 15 minutes and subsequently filtered for 10 minutes. During the filtration step the weight of the gel was reduced by 100 g. The filtercake was then divided in 3 portions, each in a 250 ml PE-bottle. To one of these bottles was added 49 g of 40% TEAOH, and the bottle was shaken for 1 minute.

The composition of the gel, expressed in terms of the molar oxide ratios, excluding water, hydrochloric acid and isopropyl alcohol, was:

1 TEA_2O : 1 Al_2O_3 : 0.075 SiO_2 : 0.98 P_2O_5.

The mixture was then transferred to a teflon-lined autoclave, and left over night on a shaking-board at room temperature. Next day the temperature was increased to 215°C, and the mixture was heated for 120 hours at this temperature. After cooling the product was washed with distilled water and centrifuged.

A portion of the product of part (a) was calcined in dry air at 550°C for 5 hours. After calcination, the SAPO-18 silico-alumino-phosphate has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 5 below.

Table 5:

2θ	d(Å)	I
9.43	9.38	vvs
10.54	8.38	s
12.84	6.89	s
13.36	6.62	w
13.86	6.39	vw
15.98	5.54	m
16.80	5.27	m
17.11	5.18	m
17.71	5.00	w
18.97	4.67	w
19.55	4.54	w
19.92	4.45	w
20.57	4.31	m
21.25	4.18	m
22.35	3.98	vw
23.03	3.96	vw
23.82	3.73	m
24.98	3.56	vw
25.88	3.44	w
26.18	3.40	w
27.71	3.22	w
29.14	3.06	vw
29.52	3.02	vw
29.92	2.98	w
30.35	2.94	w
30.63	2.92	w
31.08	2.88	m
31.53	2.84	vw
32.08	2.79	w
32.60	2.74	vw
32.95	2.72	vw
34.58	2.59	vw

The X-ray diffraction analysis revealed that the crystalline product was composed of essentially pure SAPO-18.

The composition of the solid, calcined product was established, by means of chemical analysis, as

37.2 % Al_2O_3, 1.79 % SiO_2, 61.0 % P_2O_5,

which produced a product composition, with regard to the main components, of $S_{0.02}Al_{0.45}P_{0.53}O_2$.

Example 5.

(SAPO-34.)

(a) A solution of 15.4 g of 85% phosphoric acid and 36.7 g of distilled water was added to 27.2 g of aluminium isopropoxide in a 1/4 litre PE-bottle. The bottle was shaken for 1 minute. Next 4.0 g of Ludox LS-30 colloidal silica was added, and the bottle was again shaken for 1 minute. Then 49.2 g of 40% TEAOH was added. The composition of the resulting gel, expressed in terms of the molar oxide ratios, was:

1 TEA_2O : 1 Al_2O_3 : 0.3 SiO_2 : 1 P_2O_5 : 64 H_2O: 6 C_3H_7OH.

The bottle was shaken for 1 minute, and the mixture was transferred to a teflon-lined autoclave, and left over night on a shaking-board at room temperature. Next day the temperature was increased to 215°C, and the mixture was heated for 120 hours at this temperature. After cooling the product was washed with distilled water and centrifuged. A portion of the product was calcined in dry air at 550°C for 5 hours. After calcination, the silico-alumino-phosphate mixed phase product has a crystalline structure whose X-ray powder diffraction pattern shows the following characteristic lines as indicated in Table 6 below.

Table 6:

2θ	d(Å)	I
9.41	9.39	vvs
12.82	6.90	vs
13.88	6.38	w
15.95	5.55	m
17.68	5.01	m
18.98	4.67	vw
20.55	4.32	s
21.92	4.05	vw
22.33	3.98	vw
22.99	3.87	w
24.83	3.58	m
25.86	3.44	m
27.60	3.23	vw
28.07	3.18	vw
29.48	3.03	vw
30.57	2.92	m
30.98	2.88	w
31.54	2.83	vw
33.37	2.68	vw
34.44	2.60	vw
35.91	2.50	vw
39.00	2.31	vw
39.63	2.27	vw

The X-ray diffraction analysis revealed that the crystalline product was composed of essentially pure SAPO-34.

The composition of the solid, calcined product was established, by means of chemical analysis, as

45.9 % Al_2O_3, 9.6 % SiO_2, 44.5 % P_2O_5,

which produced a product composition, with regard to the main components, of $Si_{0.095}Al_{0.533}P_{0.372}O_2$.

Example 6.

A physical mixture of SAPO-18 and SAPO-34 was prepared by mixing 1 g of the product form the first comparative example above (Example 4) with 1 g of the product form the second comparative example above (Example 5). The combined batch was mixed well, and was calcined in dry air at 550°C for 5 hours. The calcined physical mixture so obtained had an X-ray powder diffraction pattern characterized by the following characteristic lines as indicated in Table 7 below.

Table 7:

2θ	d(Å)	I
9.43	9.37	vvs
10.55	8.38	m
12.84	6.89	s
13.36	6.62	w
13.90	6.37	vw
15.98	5.54	m
16.81	5.27	m
17.13	5.17	m
17.73	5.00	w
18.99	4.67	w
19.55	4.54	vw
19.92	4.45	w
20.57	4.31	s
21.27	4.17	w
21.94	4.05	vw
22.37	3.97	vw
23.03	3.86	w
23.83	3.73	w
24.91	3.57	w
25.89	3.44	w
26.19	3.40	w
27.72	3.22	w
29.54	3.02	vw
29.96	2.98	vw
30.59	2.92	m
31.06	2.88	m
32.09	2.79	w
34.47	2.60	vw
36.03	2.49	vw
39.68	2.27	vw

A compilation of synthesis data.

Table 8. An overview of the synthesis parameters of the patent examples and the comparative examples. See below for explanation of column headings.

1	2	3	4	5	6	7	8	9	10
ex	gel Si	template/Al	phosphoric acid and water	Y/N cooling	Y/N filtration	Y/N evaporation	Y/N discharge	cryst. temp.	cryst.time hours
1	0.019	0.79	pre-mixed	0	0	0.5	0	260	2
2	0.020	1	separate	0	0	0	0.2	260	4
3	0.018	0.4	pre-mixed	0	0.4	0.3	0	260	4
4	0.018	1	separate	1	0.4	0	0	215	120
5	0.070	1	pre-mixed	0	0	0	0	215	120

The data in Table 8 are organised in 10 columns representing the following data;

1. Example number.
2. Silicon content in gel - as Si/(Si+Al+P).
3. Amount of template, TEAOH/Al-relation in gel.
4. Premixing of water and phosphoric acid: 1. Water added first and then phosphoric acid; 0.15.
5. Cooling of gel during hydrolysis of Al-isopropoxide. Yes=1, No=0.

6. Filtration of gel before template was added. Number represents fraction weight reduction.
7. Evaporating AlPO-gel by heating to < 100°C over night. Number represents fraction weight reduction.
8. Fraction and total gel discharged after sedimentation after addition of template.
9. Crystallisation temperature °C.
10. Crystallisation time in hours from heating was started.

<u>A compilation of catalyst properties.</u>

<u>Table 9.</u> An overview of phase composition and catalytic data of the patent examples and the comparative examples. For samples tested more than once, mean values are given.

1	2	3	4	5	6	7	8	9	10	11
ex	% SAPO-18	% SAPO-34	% SAPO-5	% misc	18/34	sum 18+34	h/w 4.9 Å	crystallite size	catal. life time (min)	% ethene at tDME
1	30	44	0	0	0.68	74	1	0.05	830*	47.5*
2	25	20	29	15	1.25	45	2.4	n.m	715	46.7
3	38	20	2	0	1.9	58	2	0.1	770	43.3
4	100	0	0	0		100	21	0.1	355	44.6
5	0	100	0	0	0	100	60	0.2	370*	48.4*

* Has been tested four times and the value given is the mean value. n.m.; not measured

The data in Table 9 are organised in 11 columns representing the following data;

1. Example number.
2. Content of AEI-component determined as intensity of the 5.27Å-peak (±0.02Å). Example 4 product used as reference=100%.
3. Content of CHA-component determined as intensity of the 5.55Å-peak (±0.03Å) minus the intensity of the 5.27Å-peak. Example 5 product used as reference =100%.
4. Content of AFI-component estimated from the sum of the intensities of the 19.7Å + the 22.4Å-peak. A pure and well crystalline SAPO-5 used as reference=100%.
5. Content of other phases, mostly dense quarz- or cristobalite analogues.
6. The ratio of AEI/CHA in the sample calculated from the values in columns 2 and 3.
7. Sum of AEI + CHA, i.e. column 2 + column 3. These values are referred to as "overall crystallinity" in the text but are in fact only the overall intensity of selected peaks in the diffractograms.
8. The height /width at half height of the 4.9Å peak.
9. Minimum crystal dimension as observed on SEM-micrographs, i.e. the shortest side of a crystal that can be identified as AEI or CHA by its flat square or cubic shape, respectively.
10. Catalytic lifetime in minutes, defined as the time when DME approaches 1% on carbon basis in the product stream. For samples tested more than once mean values are given.
11. Ethylene in product stream at t_{DME} measured as weight% on carbon basis.

Patent claims

1. A microporous crystalline silico-alumino-phosphate composition, the theoretical composition of which, on a water-free base after synthesis and calcination, is:

$$H_wSi_xAl_yP_zO_2$$

where w and x have a value between 0.01 and 0.05 and y and z are values between 0.4 and 0.6, wherein the composition is a mixed phase comprising silico-alumino-phosphates of AEI and CHA structure, the product after calcination in air at 550°C for 4 hours, produces a characteristic X-ray diffractogram having at least the reflections as shown in Table 1:

2 θ	d(Å)
9.3 - 9.5	9.3 - 9.4
10.4 - 10.6	8.3 - 8.5
12.7 - 12.9	6.8 - 7.0
13.8 - 14.0	6.3 - 6.4
15.9 - 16.1	5.5 - 5.6
16.7 - 16.9	5.2 - 5.3
18.9 - 19.0	4.6 - 4.7
20.5 - 20.7	4.3 - 4.4
21.0 - 21.3	4.1 - 4.3
23.7 - 24.0	3.7 -3.8
25.7 - 26.0	3.4 - 3.5
30.9 - 31.1	2.8 -2.9

2. A silico-alumino-phosphate composition according to claim 1, wherein the composition comprises at least a mixture of SAPO-34 and SAPO-18.

3. A silico-alumino-phosphate composition according to claim 2, wherein the ratios of SAPO-34 and SAPO-18 is between 4:1 and 1:4, preferably between 2:1 and 1:2.

4. A silico-alumino-phosphate composition according to claim 1, c h a r a c t e r i z e d i n t h a t it has a characteristic X-ray diffractogram as shown in table 2:

2θ	d(Å)	I
9.41	9.39	vvs
10.55	8.38	w
12.83	6.90	m
13.30	6.65	w
13.89	6.37	vw
15.96	5.55	m
16.77	5.28	w
18.94	4.68	w
19.62	4.52	vw
20.55	4.32	m
21.17	4.19	w
23.04	3.86	w
23.81	3.73	vw
25.89	3.44	w
30.99	2.88	w

5. A silico-alumino-phosphat composition according to claim 1, characterized in that it has a characteristic X-ray diffractogram as shown in table 3:

2θ	d(Å)	I
7.33	12.05	vvs
9.42	9.33	vvs
10.51	8.41	w
12.78	6.92	m
13.86	6.38	vw
14.77	5.99	w
15.97	5.54	w
16.82	5.27	w
18.96	4.68	vw
19.60	4.53	m
20.56	4.32	m
21.11	4.20	m
21.72	4.09	m
22.30	3.98	m
23.94	3.71	vw
25.79	3.45	m
28.95	3.08	vw
29.86	2.99	w
31.02	2.88	w
34.36	2.61	w
35.72	2.51	vw
37.79	2.38	vw

6. A silico-alumino-phosphate composition according to claim 1, characterized in that it has a characteristic X-ray diffractogram as shown in table 4:

2θ	d(Å)	I
7.32	12.07	w
9.44	9.36	vvs
10.53	8.40	w
12.85	6.89	m
13.34	6.63	w
13.86	6.39	vw
16.02	5.53	m
16.84	5.26	w
18.97	4.67	w
20.60	4.31	m
21.20	4.19	w
22.34	3.98	vw
23.00	3.86	vw
23.86	3.73	w
25.91	3.44	w
27.86	3.20	vw
31.04	2.88	w

7. Catalytic material comprising silico-alumino-phosphates, wherein the material comprises a mixed phase composition of SAPO-materials according to those defined in claim 1, with AEI and CHA structure in ratios between 4:1 and 1:4, preferably between 2:1 and 1:2.

8. Catalytic material according to claim 7, wherein the material comprises a mixed phase composition of SAPO-34 and SAPO-18, and the sum of SAPO-34 and SAPO-18 comprises at least 40 % of the total sample.

9. Catalytic material according to claim 7, wherein the crystal size is in the range 0,001-10 μm, preferably between 0,01- 1μm.

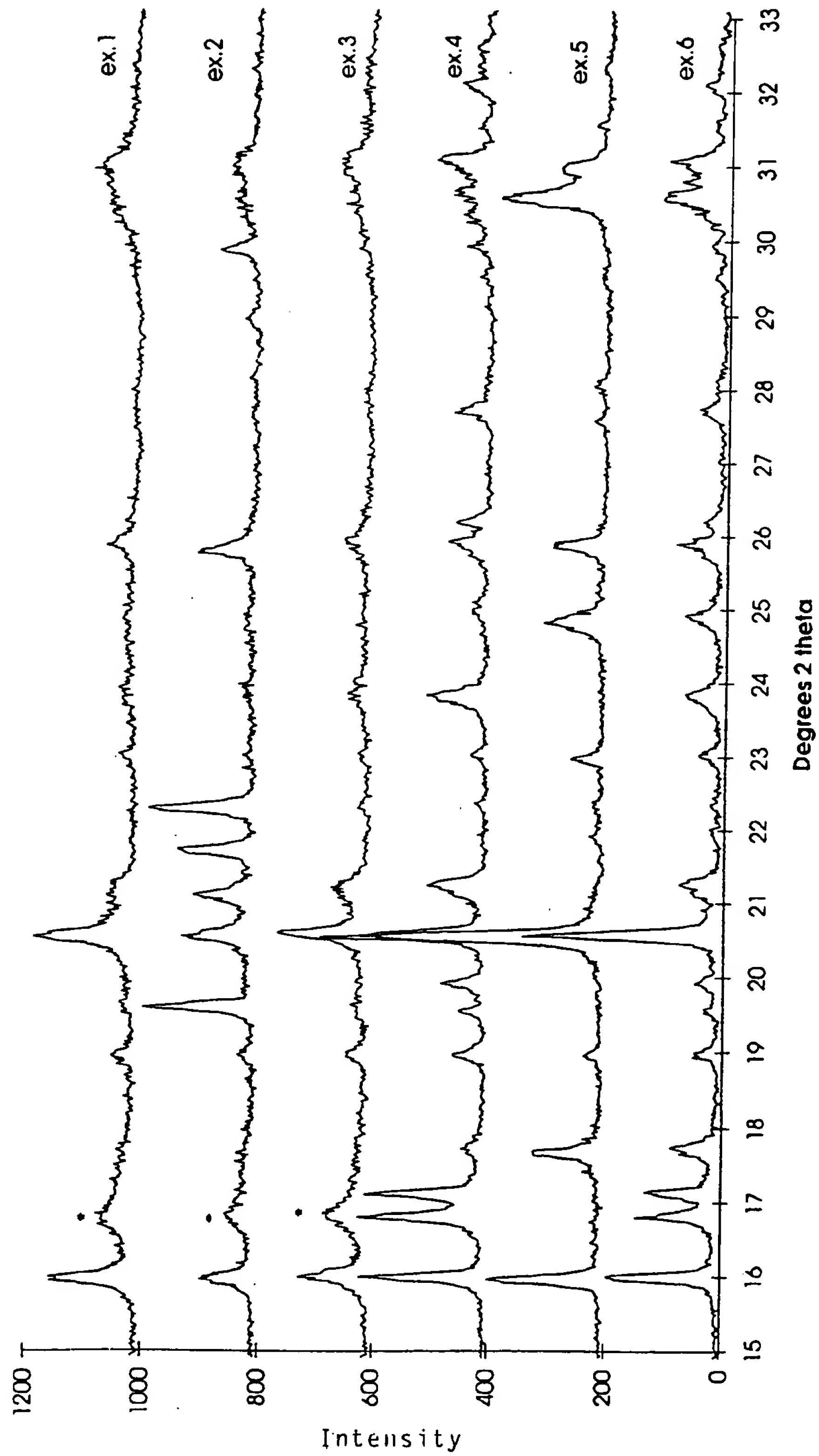
10. Catalytic material according to claim 7, wherein the height over width of the 4.9 Å-reflection is lower than for the pure phases, and preferably below 3.

11. Method for preparation of a catalytic material according to claim 7, from a mixture of reactive sources of SiO_2, Al_2O_3 and P_2O_5 and an organic template material, by combining at least one portion of the Al-source and the P-source with water, the Si-source and the organic template material,
c h a r a t e r i z e d by including one or two, but not all three, of the following steps a-c; a) addition of water and phosphoric acid, and optionally HCl to Al-isopropoxide one by one, with mixing between each addition, b) keeping the SiO_2-content below 5%, i.e. $Si/(Al+P+Si)<0.05$, c) reducing the amount of liquid after addition of the silica source.

12. Use of a product according to claim 7, as a catalyst in the production of olefins from methanol.

13. Method for the production of olefins from methanol, wherein there is used a catalyst comprising a silico-alumino-phosphate composition according to claim 7.

Fig. 1


ex.1
ex.2
ex.3
ex.4
ex.5
ex.6
Degrees 2 theta
Intensity
15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33
0 200 400 600 800 1000 1200

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 97/00272

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01B 25/45, C01B 33/26, B01J 29/02, B01J 20/16, B01J 29/06
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01B, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	US 5663471 A (STEINAR KVISLE ET AL), 2 Sept 1997 (02.09.97), abstract --	1-13
P,A	US 5609843 A (RUNE WENDELBO), 11 March 1997 (11.03.97), abstract --	1-13
A	Zeolites, Volume 11, October 1991, A.Simmen et al, "The structure determination and Rietveld refinement of the aluminiophosphate AIPO4-18", (whole article) --	1-13
A	WO 9505342 A1 (NORSK HYDRO A.S.), 23 February 1995 (23.02.95), abstract --	1-13

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 February 1998	06.02.98
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Tommy Vikholm Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 97/00272

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5437781 A (STEPHEN T. WILSON), 1 August 1995 (01.08.95), abstract -- --------	1-13

INTERNATIONAL SEARCH REPORT
Information on patent family members

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PCT/NO 97/00272

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